Phase Behavior of Living Polymer Solutions

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Calculations are provided for several essential thermodynamic properties of living polymer systems [average chain length L, average fraction of associated monomers φ, specific heat C_p, osmotic pressure Π, second virial coefficient A_2, isothermal osmotic compressibility κ, entropy S, polymerization temperature T_p, spinodal curves, and chain length distribution p(N)] using a Flory-Huggins mean-field theory. Emphasis is placed on systems having a *finite* initiator concentration r and, therefore, exhibiting a "rounded" polymerization transition, whereas previous studies primarily focus on the limit of vanishing r where the polymerization transition has been described as a second order phase transition. We find *qualitative* changes in the properties of living polymer solutions for nonzero r:

- L becomes independent of initial monomer composition φ_m^0 and temperature T at low temperatures, instead of growing without bound.
- The exponent describing the dependence of L on φ_m^0 changes by a factor of 2 from the $r \oslash 0^+$ value at higher temperatures ($T \, \varepsilon \, T_p$).
- The order parameter type variable Φ has a tail with an inflection point at T_p.
- The specific heat maximum C_p^* at T_p becomes significantly diminished, and the temperature range of the polymer transition broadens even for small r [$r \approx O(10^{-3})$].

Moreover, there are three characteristic temperatures for $r > 0$ rather than one for $r \oslash 0^+$: a "crossover temperature" T_x demarking the onset of polymerization, an r-dependent polymerization temperature T_p defined by the maximum in C_p (or equivalently, the inflection point of Φ) and a "saturation temperature" T_s at which the entropy S of the living polymer solution saturates to a low temperature value as in glass-forming liquids. Many properties of living polymer solutions are representative of other self-associating polymer systems (thermally reversible gels, colloidal gels, micelles), and we compare our results to existing experimental data.